

Appendix B

Data Quality Objectives

Planning Document

Clean Air Status and Trends Network

Data Quality Objectives

Proposed Planning Document Overview

Prepared for:
U.S. Environmental Protection Agency
Office of Air and Radiation
Research Triangle Park, NC

Prepared by:
Harding ESE, Inc.
Gainesville, Florida

February 2002

Harding ESE Project No. 311500

Data Quality Objectives

Proposed Planning Document Overview

1.0 State the Problem

1.1 Planning Team Members

The Clean Air Status and Trends Network (CASTNet) Data Quality Objectives (DQO) planning team is comprised of the Harding ESE, Inc. (Harding ESE) Project Manager, Quality Assurance (QA) Supervisor, operations managers, and other personnel with appropriate expertise as needed; the U.S. Environmental Protection Agency (EPA) QA Officer and Technical Monitors. The DQO decision makers are the Harding ESE Project Manager, QA Supervisor, and operations managers, together with the EPA Project Officer, QA Officer, and monitors. This planning team will develop and refine CASTNet DQO to support and maintain CASTNet project objectives. The decision makers have the ultimate authority to make final decisions based on the recommendations of the planning team.

1.2 Problem Description/Background

When the U.S. Congress amended the Clean Air Act in 1990, Title IV (Acid Deposition Control Program) mandated a significant reduction in the emissions of sulfur and nitrogen oxides, primarily from the electric utility industry. Titles IV and IX of the Clean Air Act Amendments (CAAA) required that the environmental effectiveness of the Acid Deposition Control Program be assessed through environmental monitoring. This monitoring was required for gauging the impact of emission reductions on air pollution, atmospheric deposition, and the health of affected human populations and ecosystems.

Prior to CASTNet, EPA operated the National Dry Deposition Network (NDDN), which was established in 1986. As with CASTNet, the objective of the NDDN was to obtain field data to establish patterns and trends of dry deposition at approximately 50 sites throughout the United States. The approach adopted by NDDN was to estimate dry deposition using measured air pollutant concentrations and modeled deposition velocities estimated from meteorological, land use, and site characteristic data. Since four to five years of data had been collected using the site locations, sampling methodology and frequencies, and equipment types established under NDDN, the same project design was used as the basis for CASTNet. CASTNet became operational in mid-1991. NDDN was incorporated into CASTNet at that time.

1.3 Resources

Published technical studies indicate that using NDDN as a guide/basis for CASTNet was a proper and cost effective strategy, especially in light of the data previously collected by NDDN. Clarke *et al.* (1997) demonstrated the accuracy and precision of CASTNet/NDDN monitoring data and Holland *et al.* (1998) demonstrated CASTNet/NDDN trend measurement sensitivity.

2.0 Identify the Decision

CASTNet's primary goal is to function effectively as a national, long-term deposition monitoring network that provides information for assessing the effectiveness of current and future emission reductions mandated under the Clean Air Act. To meet this goal, the CASTNet program was designed to fulfill the following objectives:

1. To monitor the status and trends in air quality and atmospheric deposition;
2. To provide atmospheric data on the dry deposition component of total acid deposition, rural ground-level ozone, and other forms of atmospheric pollution that enter the environment as particles and gases; and
3. To assess and report on geographic patterns and long-term, temporal trends in ambient air pollutant concentrations and acid deposition.

The network design was developed based on the assumption that dry deposition can be estimated mathematically using ambient concentrations and meteorological inputs.

2.1 DQO Trends Study Objective

The objective for trends in atmospheric sulfur and nitrogen species is a 10 percent minimum detectable trend after 10 years with a 95 percent level of confidence. This DQO was established based on the study published by Holland *et al.* (1998) that utilized CASTNet data for 34 sites in the eastern United States. Analysis of data from 1989 through 1995 demonstrated that a 10 percent trend could be detected after 10 years of data collection with a 95 percent level of confidence for sulfur dioxide (SO₂), particulate sulfate (SO₄²⁻), and nitrogen [nitric acid (HNO₃) + particulate nitrate (NO₃⁻)]. Analyses were conducted using generalized additive models (GAM) to estimate percent change per year in mean monthly concentrations. Unlike the usual linear models, GAM allow the data to suggest the form of the model. GAM were used rather than linear models to account for variables such as meteorology and seasonality. Confidence was evaluated by iterative deletion of one month of data from the total for a given site. The model estimate for a certain month using all collected data was compared with the model estimate for the same month with its data removed. The study showed that a yearly trend of less than 1.0 percent could be detected with 95 percent confidence. In other words, there is a 95 percent probability of detecting a minimum trend of 10 percent after 10 years at any particular site, for SO₂, SO₄²⁻, and nitrogen (N). The objective for trends in CASTNet data is to detect, at minimum, a 1.0 percent annual trend in concentrations after 10 years of data collection.

The CAAA Title IV Control Program mandated a 10-million ton reduction from 1980 emissions for SO₂ and a 2-million ton reduction for NO_x. In 1980, SO₂ emissions were measured at 26 million short tons¹. A 10-million ton reduction from 1980 levels would be equal to an approximate 38 percent decrease. If this reduction had been achieved in 1991 when CASTNet started, it would indicate a decrease of 4 percent per year from 1980 levels. NO_x emissions were measured at 23 million short tons in 1980². If achieved, a 2-million ton reduction would be equal to an approximate 8.7 percent decrease in 1991 or about 0.9 percent per year. Holland *et al.* (1998) demonstrated that SO₂ and N trends in airborne concentrations could be detected at 1.0 percent per year with a 95 percent level of confidence for sites in the eastern United States. For western sites, low site density and low concentrations prevent

¹ <http://www.epa.gov/oar/emtrnd94/tres.pdf>

² Ibid.

extrapolation of this result. However, since the U.S. Congress is the de facto decision-maker as regards the reductions required by CAAA Title IV, the 4 percent SO₂ and 1 percent NO_x decisions still apply for western sites. More data from western sites, including appropriate geography and wind patterns, are needed to make a reasonable determination of the sensitivity of trend calculations for this region.

2.2 Additional DQO

Spatial patterns are also desired for policy decision-making. Initial study into formulation of a spatial pattern DQO was performed by Dr. William Tucker of Harding ESE. The Technical Memorandum resulting from this initial study is attached as Appendix A.

Uncertainties in the computer model have not been sufficiently quantified to determine a DQO for deposition flux.

3.0 Identify the Inputs to the Decision

Parameters used by the computer model for CASTNet/NDDN are listed in the table below:

Measurement Parameter	Medium	Method
Wind Speed	Continuous Ambient Monitoring	Anemometer
Wind Direction	Continuous Ambient Monitoring	Wind Vane
Sigma Theta	Continuous Ambient Monitoring	Wind Vane
Relative Humidity	Continuous Ambient Monitoring	Thin Film Capacitor
Solar Radiation	Continuous Ambient Monitoring	Pyranometer
Precipitation	Continuous Ambient Monitoring	Tipping Bucket Rain Gauge Weighing Rain Gauge
Ambient Temperature	Continuous Ambient Monitoring	Platinum RTD
Surface Wetness	Continuous Ambient Monitoring	Conductivity Bridge
O ₃	Continuous Ambient Monitoring	Ultraviolet Absorbance
Filter Pack Flow*	Continuous Ambient Monitoring	Mass Flow Controller
Ammonium (NH ₄ ⁺)	Filter Pack Samples	Automated Colorimetry
Sodium (Na ⁺)	Filter Pack Samples	ICAP-AE
Potassium (K ⁺)	Filter Pack Samples	ICAP-AE
Magnesium (Mg ²⁺)	Filter Pack Samples	ICAP-AE
Calcium (Ca ²⁺)	Filter Pack Samples	ICAP-AE
Nitric Acid (HNO ₃)	Filter Pack Samples	Ion chromatography
Nitrate (NO ₃ ⁻)	Filter Pack Samples	Ion chromatography
Sulfate (SO ₄ ²⁻)	Filter Pack Samples	Ion chromatography

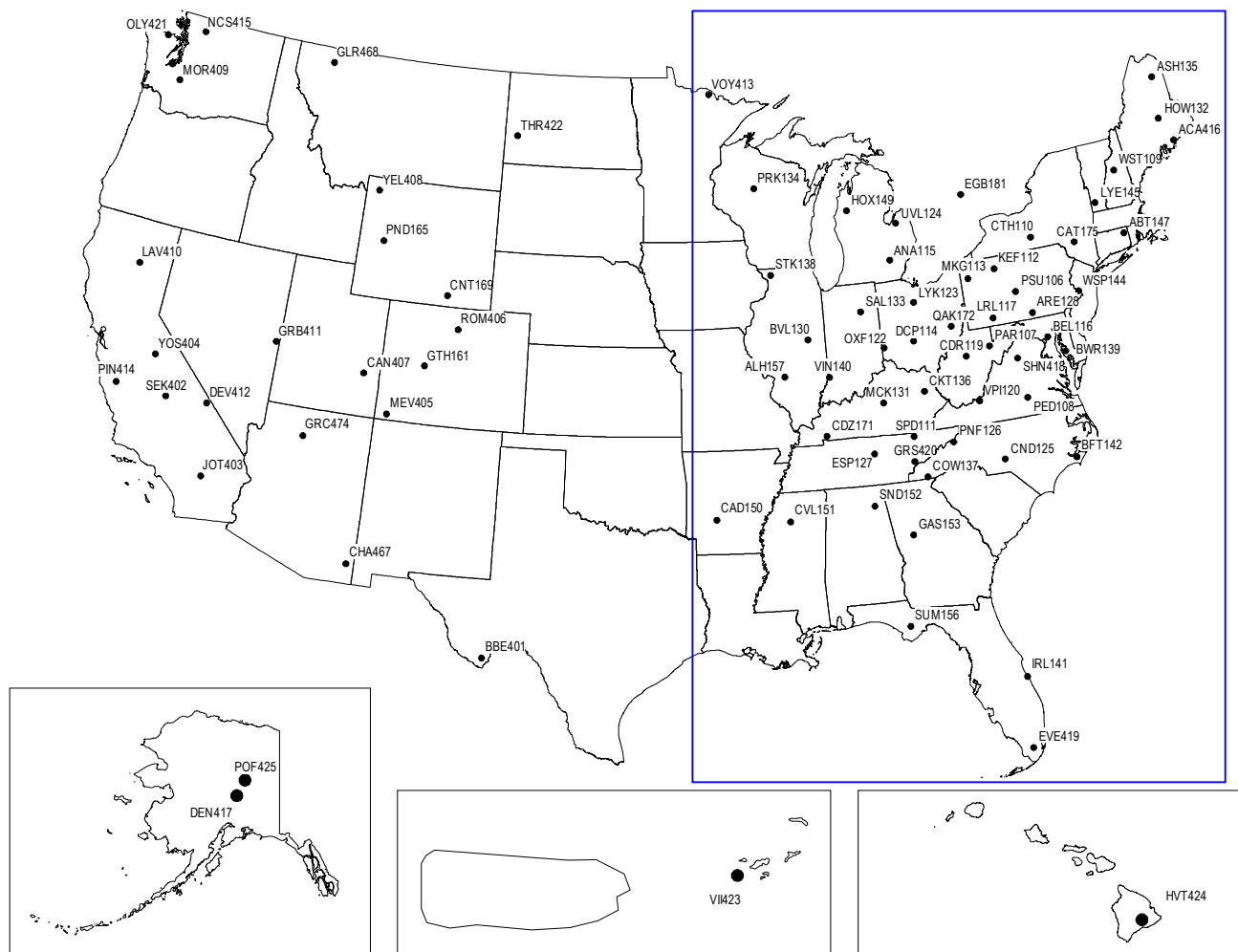
Note: *Flow rate is used along with filter pack sample measurements to calculate atmospheric concentrations. The calculated atmospheric concentrations are then used in the model.

ICAP-AE = inductively coupled argon plasma-atomic emission

RTD = resistance-temperature device

4.0 Define The Study Boundaries

The study boundaries would encompass the entire network for site-by-site concentration trends and future study to quantify deposition and spatial distribution within the network. Current CASTNet site locations are indicated on the following map. Only the sites located within and to the east of the line of states extending from Minnesota in the north to Louisiana in the south (outlined in blue) would comprise the study area for determination of complete DQO for concentration trends and spatial distribution of SO₂.



5.0 Develop a Decision Rule

The accuracy of reported CASTNet concentration data allow measurement of a minimum annual change of 1.0 percent for SO₂, SO₄²⁻, and N at a given site in the eastern region with a statistical confidence of 95 percent. Spatial distribution maps for SO₂ are accurate with 90 percent confidence for eastern sites.

6.0 Specify Tolerable Limits on Decision Errors

6.1 Sulfur Dioxide, Particulate Sulfate, and Nitrogen

Limits on decision errors for SO₂, SO₄²⁻, and N are indicated by the study published by Holland *et al.* (1998) that utilized CASTNet data from 1989 through 1995 for 34 sites in the eastern United States. Analysis of these data demonstrated that an approximate 1.0 percent trend could be detected per year with a 95 percent level of confidence. In other words, there is a 95 percent probability of detecting a minimum trend of 10 percent after 10 years at any particular site, for SO₂, SO₄²⁻, and N at eastern sites.

6.2 Ozone

Limits on decision errors for ozone (O₃) are based on analysis of historical O₃ calibration results at eastern sites. All calibrations were performed using EPA traceable standards, which provide a good indication of analyzer accuracy. The data show that 98 percent of all calibrations on record from January 1989 through October 2001 were within the established ± 10 percent criterion (i.e., calibration curve slopes were between 0.90 and 1.10) and 97 percent were within the ± 5 percent criterion (slopes were between 0.95 to 1.05). Calibration results for all collocated sites (approximately 106, paired) for the same period yielded a measured precision of 3 percent. Using the following propagated uncertainties:

Analyzer accuracy = 5% or 0.05

Network precision = 3% or 0.03

$$\text{Total Propagated Uncertainty (TPU)} = \text{SQRT}[(0.05)^2 + (0.03)^2] = 0.06 \text{ or } 6\%$$

These data indicate that trends above 6 percent can be detected after approximately 13 years with a 97 percent confidence level. For the sake of simplicity, the stated DQO for O₃ will match the sulfur and nitrogen species DQO (i.e., 10 percent minimum detectable trend after 10 years with 95 percent confidence).

6.3 Spatial Distribution of SO₂

Spatial distribution maps for SO₂ in the eastern United States show a real pattern with 90 percent confidence that the maximum interpolated value is greater than the minimum interpolated value. This applies to the area shown on the map as a whole. More analysis is needed to establish accuracy for a given locality within the mapped region. The test for local areas will likely involve analysis of absolute errors in the kriging estimates as compared with the estimated geometric means for the region as described in Appendix A.

6.4 Dry Deposition

A DQO for trends in dry deposition is not practical at this time. Although Meyers *et al.* (1998) and Finkelstein *et al.* (2000) demonstrated that the MLM is essentially unbiased for flat, non-forested settings, the uncertainties in the MLM have not been sufficiently quantified for establishing a definitive DQO.

6.5 Other Measurements

As stated previously, more data are needed to quantify accuracy and uncertainties in all measurements at western sites.

In addition, more analysis is needed to determine a spatial patterns DQO for all pollutants. More analysis should yield quantification at greater resolution than is currently shown.

7.0 Optimize the Design

Since NDDN sites were transferred to CASTNet at the beginning of the project, initial network and site design were necessarily driven by the prior design of NDDN and the 4 to 5 years of data collection already performed. Site design and sampling methodology have largely been dictated by this and by computer model requirements. Sampling duration and frequency were selected for increased comparability with other networks such as the National Oceanic and Atmospheric Administration's (NOAA) Atmospheric Integrated Research Monitoring Network (AIRMoN). The selection of the parameters measured and completeness requirements are all model-driven. Factors not driven by model requirements, such as regional site density, may allow for further optimization if research shows that project objectives may still be met. For example, automated sequential samplers may reduce costs if it is determined that filter packs can remain on the tower for a certain period after sampling is complete, thus reducing site operator visits. The spatial pattern estimation, as noted in Dr. William Tucker's technical memorandum (Appendix A), may be optimized for cost with further research into the level of site densities required per region to achieve a certain minimum accuracy of kriging estimates.

References

- Clarke, J.F., Edgerton, E.S., Martin, B.E. 1993. Dry Deposition Flux Calculations for the Clean Air Status and Trends Network. *Atmospheric Environment*. 31:3667-3678.
- Finkelstein, P.L., Ellestad, T.G., Clarke, J.F., Meyers, T.P., Schwede, D.B., Hebert, E.O., and Neal, J.A. 2000. Ozone and Sulfur Dioxide Dry Deposition to Forests: Observations and Model Evaluation. *JGR*. 105:D12:15,365-15,377.
- Holland, D.M., Principe, P.P., and Sickles, J.E. 1998. Trends in Atmospheric Sulphur and Nitrogen Species in the Eastern United States for 1989-1995. *Atmospheric Environment*. 33:37.
- Meyers, T. P., Finkelstein, P., Clarke, J., Ellestad, T.G., and Sims, P.F. 1998. A Multilayer Model for Inferring Dry Deposition Using Standard Meteorological Measurements. *J. Geophys. Res.*, 103D17:22,645-22,661.